

Electrodialysis of LiPF_6 in Aqueous Solution for Wastewater Treatment in Hydrometallurgical Recycling of Lithium-Ion Batteries

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In the deactivation of spent lithium-ion batteries (LIBs) by crushing in water for small-scale recycling, one of the most difficult challenges is the treatment of wastewater containing LiPF_6 due to the slow decomposition rate of PF_6^- . Additionally, the recovery of dissolved Li^+ in wastewater is required. This study aims to separate PF_6^- and Li^+ from wastewater containing LiPF_6 by electrodialysis. LiPF_6 solution is prepared as the feed, and PF_6^- and Li^+ are transferred into the anolyte and catholyte through an anion exchange membrane (AEM) and a cation exchange membrane (CEM), respectively. The transport numbers of PF_6^- and Li^+ in the AEM and CEM are measured as 0.22–0.32 and 0.22–0.50, respectively. Then, the effects of the compounds derived from LIBs electrolyte, ethylene glycol, and formic acid on the electrodialysis are investigated. In addition, the transport chemistry of LiPF_6 is discussed by comparing the electrodialysis of LiPF_6 with that of NaCl . The higher permselectivity of PF_6^- in the AEM is explained by the hydrophobicity of anions. Finally, the operation costs of wastewater treatment are estimated. This estimation suggests that electrodialysis has the potential to significantly reduce the cost of wastewater treatment.

1. Introduction

The amount of spent lithium-ion batteries (LIBs) is predicted to increase rapidly in the future, and various recycling processes of spent LIBs are proposed.^[1–3] The recycling process is complicated by the need to separate the numerous elements contained in LIBs and treat the flammable organic solvents and potentially

harmful fluorine to environment. Typical recycling process of spent LIBs is designed to prioritize the recovery of cobalt (Co), nickel (Ni), and copper (Cu), which have high market values. A relatively large-scale recycling process, led by Umicore (Belgium), is the pyrometallurgical process.^[4,5] In this process, Co and Ni are recovered as alloys by reduction at high temperatures above 1200 °C, where the slag phase and metal phase equilibrate. In this process, aluminum (Al) and manganese (Mn) are incorporated into the slag. Lithium (Li) is typically incorporated into the slag, but in the recent method reported by Umicore, Li is recovered from the flue dust.^[5] Because of the large scale of this process, recycling plants are localized, and transportation and storage of spent LIBs are required. LIBs must be handled as hazardous materials during transport and storage according to regulations,^[6] and there have been many reported

cases of fires caused by improper handling.^[7] Once LIBs ignite, the spraying of water may contribute to the fire, resulting in longer extinguishing times and more damage.^[8]

In contrast to pyrometallurgical process, recovery of valuable elements from black mass, the mixed powder of cathode and anode materials, is conducted by deactivating and crushing the LIBs below or near the melting point of Al.^[9] In this process, Co, Ni, and Mn are recovered from leachate of black mass, and Li is recovered from the residual leachate. In deactivation of LIBs, the reduction of the explosion risk due to the high energy density and flammable electrolyte^[10] is the most important. Major methods of deactivation include pyrolysis, discharge, and crushing in an inert environment.^[9,11] In deactivation by pyrolysis, the electrolyte is removed by evaporation or combustion. The disadvantage of pyrolysis is that fluorine-containing gases are generated, and large facilities for the treatment of exhaust gas are needed. Deactivation by discharge is performed, for example, by immersion in salt water, but the slow rate of deactivation, the generation of hydrogen and chlorine gas, and the leakage of electrolyte due to corrosion of LIBs components are problematic.^[12,13] As a deactivation method by crushing, the crushing in water was proposed by Asaka Riken, maybe for the first time.^[14] Our group improved the crushing in water by conducting in inert atmosphere to reduce the risk of hydrogen explosion and fire.^[15] This method enables deactivation of LIBs with relatively small-scale facilities, resulting in lower initial investment and energy consumption.

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One of the most difficult challenges for the crushing in water is the treatment of wastewater containing electrolytes of LIBs. The main components of the electrolyte are carbonate ester as a solvent and lithium hexafluorophosphate (LiPF_6) as a Li salt. Typical carbonate ester used in LIBs electrolyte is ethylene carbonate, propylene carbonate, and dimethyl carbonate. In alkaline solutions, most of these carbonates are rapidly hydrolyzed to alcohols such as ethylene glycol (EG) and ethanol.^[16,17] Alcohols are then treated by oxidation to decompose into carbon dioxide.^[18] On the other hand, the treatment of LiPF_6 is known to be difficult due to the high kinetic stability of PF_6^- in water. Studies on wastewater treatment reported that PF_6^- is particularly difficult to decompose and even detected in tap water in some areas.^[19,20] The simplest method for the removal of PF_6^- is to spray burn the wastewater, but this requires combustion equipment and fuel, which offsets small-scale merits of the method of crushing in water. As another method for decomposition of PF_6^- , the addition of strong acids^[21–23] or aluminum salts^[24,25] at elevated temperature and precipitation by adding $\text{Ca}(\text{OH})_2$ has been proposed. This treatment requires higher costs for chemical reagents and heating, depending on the volume of wastewater. Therefore, it is necessary to concentrate and reduce the volume of wastewater containing PF_6^- .

Another challenge in the method of crushing in water is the recovery of Li. The EU Battery Regulation sets the targets for recovery of Li at 50% and 80% no later than the end of 2027 and 2031, respectively.^[26] In case spent LIBs are deactivated by crushing in water, Li in the cathode material is distributed to the black mass, which can be recovered in the subsequent process. In contrast, Li in the anode material and electrolyte is dissolved as Li^+ in water used for crushing. To achieve a high total recovery rate, Li dissolved in water needs to be recovered. The recovered lithium is commercialized in the form of lithium carbonate (Li_2CO_3) or lithium hydroxide (LiOH), and the separation and concentration of Li^+ in water is required.^[27]

The application of electrodialysis is expected to simultaneously solve the problems of concentration of PF_6^- and separation of Li^+ . In electrodialysis, cations and anions are separated by electrophoresis across ion exchange membranes (IEM). The technique of electrodialysis is used for desalination of seawater,^[28,29] industrial wastewater treatment,^[30–32] process of food production,^[33] and so on. For example, in seawater desalination, cation exchange membranes (CEMs) and anion exchange membranes (AEMs) are arranged alternately, and a voltage is applied at both ends as shown in Figure 1 (a). Along with the electrode reactions on anode and cathode, sodium ions (Na^+) and chloride ions (Cl^-) are selectively separated by CEMs and AEMs, respectively, and diluted and concentrated NaCl solutions are produced. When separate recovery of cations and anions is required, bipolar electrodialysis is used as shown in Figure 1 (b).^[34,35] Bipolar membrane (BPM) is a composite membrane of an AEM and a CEM, and the application of voltage causes water dissociation inside BPM and produces hydrogen ions (H^+) and hydroxide ions (OH^-). BPMs, CEMs, and AEMs are arranged in sequence, and voltage is applied at both ends. Several studies have reported the concentration of Li^+ by electrodialysis for spent LIBs recycling.^[35–38] These studies reported Li^+ recovery from a leachate for the black mass and focused on the separation of Li^+ from other cations such as Co^{2+} and Ni^{2+} . Aiming at the concentration

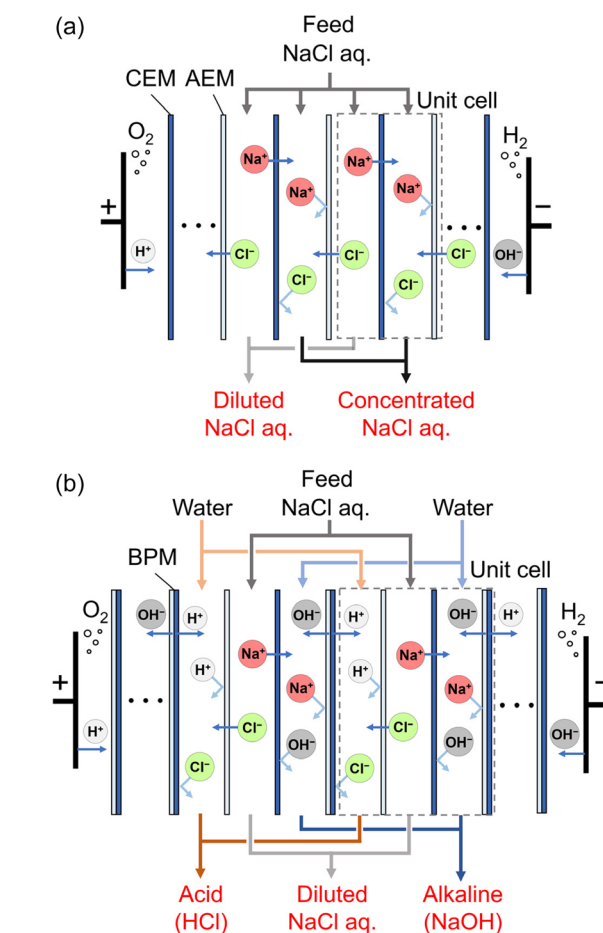


Figure 1. Schematic illustration of a) electrodialysis and b) bipolar membrane electrodialysis.

of Li^+ from sea water, methods for separation of Li^+ from other cations such as Na^+ , Mg^{2+} , and Ca^{2+} have been investigated by many researchers such as surface modification treatment of the CEM,^[39] impregnation of ionic liquid into the CEM,^[40] and lithium lanthanum titanate as fast Li^+ conductor.^[41]

In this study, the separation and concentration of Li^+ and PF_6^- from LiPF_6 solution by electrodialysis were attempted using commercially available hydrocarbon-based membranes, Selemion DSVN and CMVN (AGC Inc.). In deactivation by submerged crushing in water, metal cations other than Li^+ basically do not dissolve from LIB electrolyte in water, and relatively easy recovery of Li^+ is expected. On the other hand, to the best of our knowledge, the concentration of PF_6^- by electrodialysis has not been reported. The structure and ionic radius of PF_6^- are relatively different from typical inorganic anions, but its permeation behavior at an AEM is not reported. In addition, the effects of the presence of other electrolyte-derived compounds on electrodialysis need to be elucidated. The impurities considered in this work were EG and HCOOH , which are representative compounds formed by the decomposition of carbonate esters in LIBs electrolyte. In order to investigate the chemistry of LiPF_6 in electrodialysis, it was compared to NaCl electrodialysis. The transport numbers were measured for LiPF_6 and NaCl

electrodialysis as individual solutions and mixed solution. The comparison with NaCl is significant not only for academic purposes, but also as an investigation of the effect of contamination since NaCl is expected to be easily contaminated by various factors. The experiment was conducted by circulating anolyte, feed, and catholyte in three chambers separated by a single AEM and CEM, respectively. In the actual process, a setup of multiple unit cells as shown in Figure 1 is desirable, but in this study, for simplicity, the experiment was conducted with a single unit cell.

2. Experimental Section

Electrodialysis was performed using a commercially available cell (AGC Inc., DW-LAB) as shown in Figure 2 (see also Supporting Information [A]). Three chambers were separated by a CEM (Selemon CMVN, AGC Inc.) and an AEM (Selemon DSVN, AGC Inc.). The comparison of AEMs in the view of membrane resistance is shown in Supporting information [B]. Since PF_6^- permeated AEM with relatively high membrane resistance, DSVN, a membrane with lower membrane resistance, was used. It should be noted that DSVN is a membrane designed for diffusion dialysis, which may allow H^+ permeation. The SUS316 (effective surface area: 25 cm^2) plate and iridium (Ir)-coated titanium (Ti) plate (effective surface area: 25 cm^2) were used as cathode and anode, respectively. The dimensions of each chamber were 3 mm thick, 5 cm wide, and 6 cm long, and effective surface areas of the CEM and the AEM were 30 cm^2 . The electrolyte pumped into the chamber between the CEM and the AEM was called “feed” in this study. The electrolyte on the anode and cathode side is called “anolyte” and “catholyte”, respectively. The electrolyte compositions at each condition are shown in Table 1. Reagents used for preparation were LiPF_6 (Fujifilm Wako Pure Chemical Corporation, 98.0 + %), Na_2SO_4 (Nacalai Tesque, Inc., GR), $\text{LiOH}\cdot\text{H}_2\text{O}$ (Nacalai Tesque, Inc., SP), EG (Fujifilm Wako Pure Chemical Corporation, 99.5 + %), HCOOH (Fujifilm Wako Pure Chemical Corporation, 98.0 + %), NaCl (Nacalai Tesque, Inc., GR), and LiCl (Nacalai Tesque, Inc., GR).

Table 1. Electrolyte compositions used in the electrodialysis experiments. ($M = \text{mol L}^{-1}$).

Exp. #	Feed [1000 mL]	Anolyte [70 mL]	Catholyte [70 mL]
01	50 mM LiPF_6	50 mM Na_2SO_4	100 mM LiOH
02	50 mM LiPF_6 + 10000 C-ppm EG	50 mM Na_2SO_4	100 mM LiOH
03	50 mM LiPF_6 + 50 mM HCOOH	50 mM Na_2SO_4	100 mM LiOH
04	50 mM NaCl	50 mM Na_2SO_4	100 mM LiOH
05	50 mM LiPF_6 + 50 mM NaCl	50 mM Na_2SO_4	100 mM LiOH

The preparation method of the electrolyte is already reported in our previous report.^[25] The electrolytes were circulated through respective chambers by tubing pumps (As One corp., Front lab tubing pump) at a flow rate of 115 mL min^{-1} at room temperature. A constant current of 1000 mA (40 mA cm^{-2} on the electrodes and 33 mA cm^{-2} on the membranes) was applied between the anode and cathode using a potentiogalvanostat (Solartron Analytical, solartron 1287). The changes of cell voltage were recorded by a multi-channel data logger (Agilent Technologies, Agilent 34972A). About 1 mL of electrolytes was sampled after 1-hour electrodialysis, and the concentrations of phosphorus (P), Li, Na, and sulfur (S) were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Hitachi High-Tech Science Corporation, SPS3520UV). The electrodialysis was performed for 3 h, and the solutions were sampled for analysis at 0, 1, 2, and 3 h of electrodialysis time. When the solution contained both Na and Li, the influence of interference between alkali metals in ICP-AES measurement can be reduced by turning off the flow of chamber gas of the instrument (see Supporting information [C]). The correlation coefficients of the calibration curves for P and Li were greater than 0.9998 and 0.999, respectively. ICP-AES measurements were performed twice per sample, and the average values were used as the result. The raw data of the measurements are shown in Supporting information [D]. The sampled electrolytes were also measured by ion chromatography (Shimadzu Corporation, HIC-ESP). The measurement results of ion chromatography

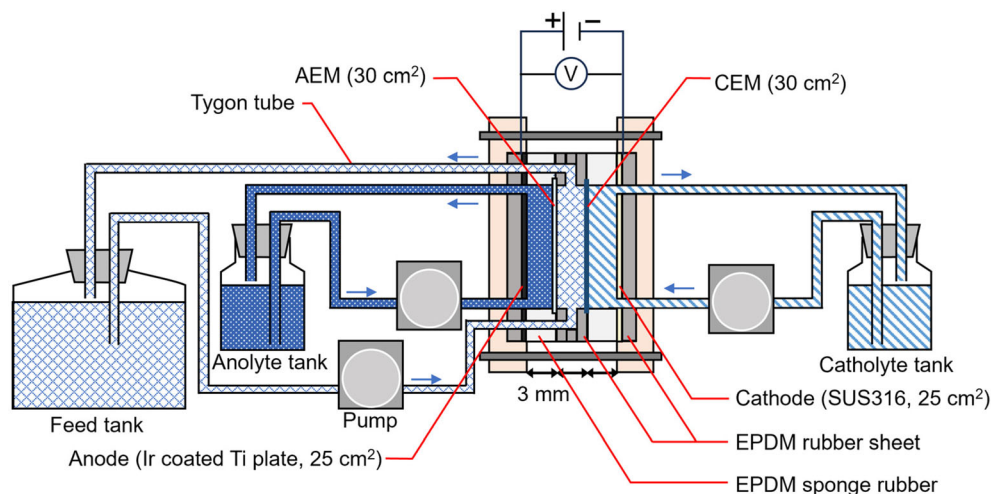


Figure 2. Schematic illustration of the electrodialysis cell.

showed that all of P in the electrolyte existed in the states of PF_6^- (see Supporting information [E]). The transport number was calculated using the measurement results by ICP-AES. Only for Cl^- and HCOO^- , the measurement results of ion chromatography were used. Total organic carbon analyzer (Shimadzu Corporation, TOC-L) was used for measurement of the concentration of EG.

3. Calculation of Transport Number of Each Ion in the AEM and the CEM

In this study, transport numbers are defined as the proportion of charge transfer by the ion transport to the total current. Given the above, the transport number is obtained from the amount of each ion permeated and total charge amount as expressed in Equation (1)^[42]

$$t_i^m = \frac{zF\Delta n}{It} \quad (1)$$

in which t_i^m is the transport number of ion i , z is the charge of ion i , F ($= 96485 \text{ C mol}^{-1}$) is Faraday constant, Δn [mol] is the amount of substance of ion i that permeated the membrane, I [A] is current, and t [s] is electrodialysis time. The transport number calculated according to Equation (1) is occasionally referred to as the current efficiency. Detailed transport number calculations for each ion are given below.

3.1. Transport Number of Each Ion in the AEM

The transport number of each anion in the AEM was calculated from the decrease in concentration of each anion in the feed ($C_A^{\text{Feed}} (>0)$) according to Equation (2).

$$t_A^{\text{AEM}} = \frac{VF}{It} \Delta C_A^{\text{Feed}} \quad (A = \text{PF}_6^-, \text{Cl}^-, \text{HCOO}^-) \quad (2)$$

In the electrodialysis performed in this study, OH^- was assumed to be responsible for the rest of charge transfer in the AEM, and the value of $t_{\text{OH}^-}^{\text{AEM}}$ was calculated according to Equation (3).

$$t_{\text{OH}^-}^{\text{AEM}} = 1 - \sum_A t_A^{\text{AEM}} \quad (A = \text{PF}_6^-, \text{Cl}^-, \text{HCOO}^-) \quad (3)$$

3.2. Transport Number of Each Ion in the CEM

Transport numbers in the CEM were calculated in the same manner. The transport number of Li^+ , Na^+ (only in exp. #04 and #05), and H^+ was calculated from the decrease in concentration of each cation in the feed ($C_C^{\text{Feed}} (>0)$) according to Equation (4) and (5).

$$t_C^{\text{CEM}} = \frac{VF}{It} \Delta C_C^{\text{Feed}} \quad (4)$$

$$t_{\text{H}^+}^{\text{CEM}} = 1 - \sum_C t_C^{\text{CEM}} \quad (C = \text{Li}^+, \text{Na}^+) \quad (5)$$

3.3. Effects of Coions Permeation and Water Osmosis on Transport Number

In the evaluation of the transport number in this study, the effects of coion permeation and water osmosis were considered as follows. In an ideal IEM, only counterions against fixed charges permeate the membrane, that is, anions for the AEM and cations for the CEM. In an ideal IEM, only the ions that are opposite to the charge of fixed ionic group can permeate. For example, in an AEM, anions permeate, while in a CEM, cations permeate. However, in reality, some ions with the same charge as the fixed ionic groups and even water can also leak through the membrane. The coions permeation in this study was evaluated, and the transport number of Na^+ in the AEM (permeation from an anolyte to a feed) was about 0.04 at the highest value (see Supporting information [F]). This value is relatively low enough, and the coions permeation is assumed to be ignored in this study. For water osmosis, two main factors were reported: osmosis water transfer caused by concentration and pressure differences on both sides of the IEM and electro-osmosis water transfer caused by the movement of hydrated water associated with the ion permeation.^[43,44] The amount of water osmosis in this study was estimated to be at most 10 mL (see Supporting Information [G]). The influence of water permeation was ignored by the large solution volume relative to the water permeation volume when calculating the transport number from the concentration change of the feed.

3.4. Measured and Calculated Value of pH before and after Electrodialysis

The value of pH in each electrolyte before and after electrodialysis was measured by a pH electrode (Horiba, Ltd., 9632-10D). In addition, the calculated value of pH was obtained from the transport number of H^+ and OH^- according to ESI [H].

4. Results

4.1. Electrodialysis of LiPF_6 Solution without Additives

The electrodialysis of LiPF_6 solution without additive was performed using 50 mM LiPF_6 solution as a feed (exp. #01). The change in concentration of PF_6^- and Li^+ is shown in Figure 3 (a) and (c), respectively. To evaluate the mass balance in different volumes of solutions, the amount of substance is also shown in Figure 3 (b) and (d). The concentration of PF_6^- decreases in the feed and increases in the anolyte, and the concentration of Li^+ decreases in the feed and increases in the catholyte. Clearly, these results show that PF_6^- and Li^+ in the feed are transported into the anolyte and catholyte, respectively. The transport number of each ion in the AEM and CEM is shown in Figure 4. The transport number of PF_6^- in the AEM and Li^+ in the CEM is in the range of 0.22–0.32 and 0.20–0.50, respectively. These transport numbers decrease following the electrodialysis time. The decreases in transport numbers are attributed to the decrease in the concentrations of PF_6^- and Li^+ in the feed during the electrodialysis. As shown in Figure 5, the measured and calculated values of pH in the feed and anolyte became acidic

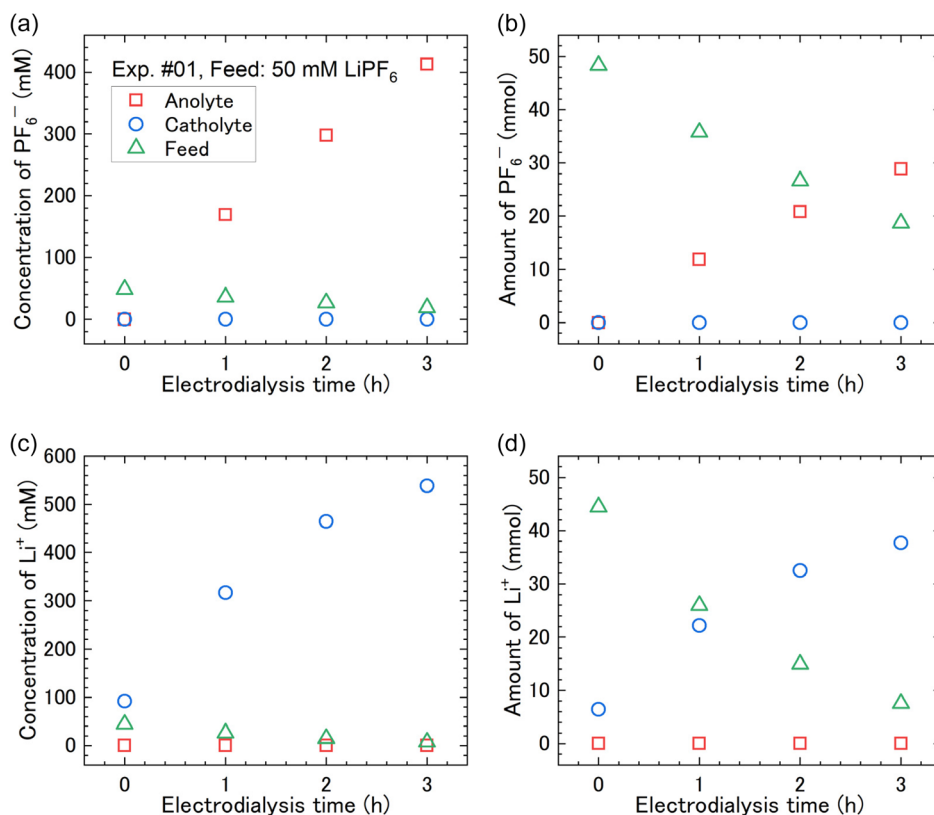


Figure 3. The changes of concentration and amount of a), b) PF_6^- and c), d) Li^+ for exp. #01, where the electrodialysis was performed at 1000 mA (40 mA cm^{-2} on the electrodes and 33 mA cm^{-2} on the membranes) using 50 mM LiPF_6 as the feed (1000 mL), $50 \text{ mM Na}_2\text{SO}_4$ as the anolyte (70 mL), and 100 mM LiOH (70 mL) as the catholyte.

near pH 2 and 0–1 with electrodialysis, respectively, in which the measured and calculated values coincided. Catholyte is alkaline with pH 12–14, and the slight differences between measured and calculated values are expected to be due to alkaline error in measuring pH with the glass electrode.

4.2. Effect of EG and Formic Acid

The electrodialysis of LiPF_6 solution containing EG was performed using $50 \text{ mM LiPF}_6 + 10000 \text{ C-ppm EG}$ solution as the feed (exp. #02). The changes of transport numbers of PF_6^- and Li^+ and pH were almost the same as those without EG as shown in Figure 6 (a) and (b). See Supporting information [H] for data on concentration changes used to obtain transport numbers. The concentration changes of EG in each electrolyte are shown in Figure 6 (c). To discuss the low-concentration region of EG, the enlarged view is shown in Figure 6 (d). The concentrations of EG in the anolyte and catholyte increase with the electrodialysis time. The diffusion from the feed into these solutions is expected to occur by concentration differences.

Next, the electrodialysis of LiPF_6 solution containing formic acid was performed using $50 \text{ mM LiPF}_6 + 50 \text{ mM HCOOH}$ solution as feed (exp. #03). The transport numbers PF_6^- and Li^+ and pH were scarcely affected by the addition of formic acid, as

shown in Figure 7. See Supporting information [I] for data on concentration changes used to obtain transport numbers. The transport number of HCOO^- in the AEM is relatively low, ranging from 0.02 to 0.06. The fact that most of the formic acid ($\text{pK}_a = 3.75$ at 20°C)^[45] was in an undissociated state (HCOOH) due to the low pH in the feed (around pH 2) is a possible reason for the low transport number.

These results indicate that EG and formic acid produced by the decomposition of LIB electrolyte do not significantly affect the PF_6^- and Li^+ separation by electrodialysis. The effects of small amounts of permeated organic compounds on the subsequent process need to be investigated in the future.

4.3. Comparison with NaCl Electrodialysis

The transport numbers of PF_6^- in the AEM and Li^+ in the CEM were compared with those of Cl^- in the AEM and Na^+ in the CEM, respectively. The electrodialysis was performed using 50 mM NaCl solution (exp. #04) and $50 \text{ mM LiPF}_6 + 50 \text{ mM NaCl}$ (exp. #05) as the feeds. Transport numbers in the AEM and the CEM at 0–1 h of electrodialysis time range in exp. #01, #04, and 05 are shown in Figure 8. The comparison of exp. #01 and #04 obviously shows that the transport number of Cl^- in the AEM is larger than PF_6^- when each ion permeates the AEM singly. However, when they coexist in the same amount

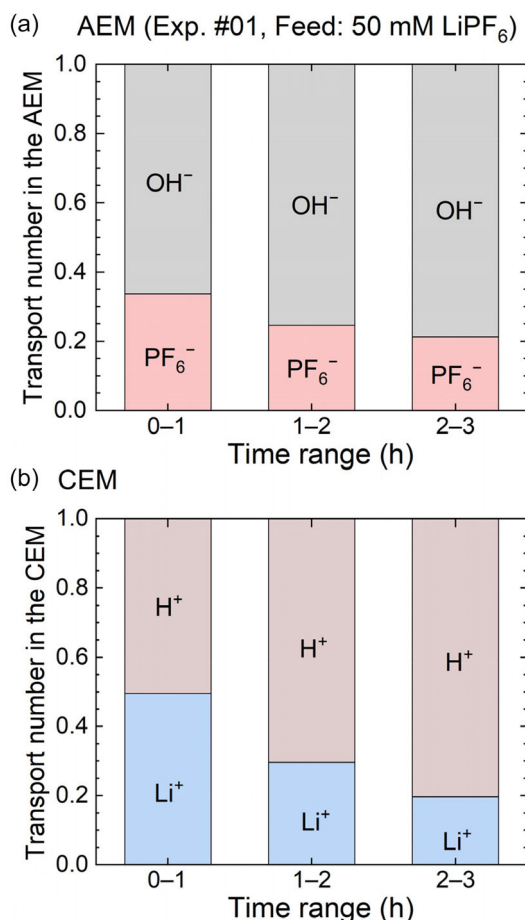


Figure 4. The transport numbers in a) the AEM and b) CEM for exp. #01, where the electrodialysis was performed at 1000 mA (40 mA cm^{-2} on the electrodes and 33 mA cm^{-2} on the membranes) using 50 mM LiPF_6 as the feed (1000 mL), 50 mM Na_2SO_4 as the anolyte (70 mL), and 100 mM LiOH (70 mL) as the catholyte.

in the feed in exp. #05, the transport number of Cl^- is lower than PF_6^- . This result is discussed in the next section.

For cations, transport numbers in the CEM are $\text{Na}^+ > \text{Li}^+$ in both cases of single and simultaneous permeation, as shown in Figure 8 (b). Among homologous cations in the periodic table, the cation with the smaller ionic Stokes radius ($\text{Na}^+ = 1.84 \text{ \AA}$, $\text{Li}^+ = 2.83 \text{ \AA}$)^[46] was reported to preferentially permeate the AEM.^[42,47] The result in Figure 8(b) is explained by this property.

5. Discussion

5.1. Transport of OH^- in the AEM

In this study, the transport numbers of PF_6^- and Cl^- in the AEM were obtained by the concentration changes in the feed, and the transport number of OH^- is calculated by assuming that they are responsible for the rest of charge transfer. This assumption is probably correct since the pH calculated based on this assumption is equal to the measured pH as shown in Figure 5. However, in this study, the value of pH in the feed was around 2–3, and

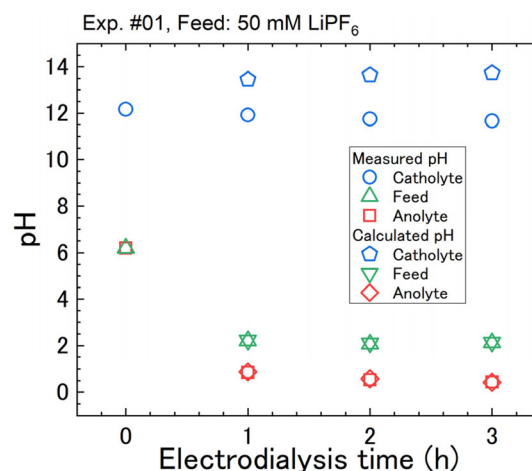


Figure 5. Measured and calculated values of pH for exp. #01, where the electrodialysis was performed at 1000 mA (40 mA cm^{-2} on the electrodes and 33 mA cm^{-2} on the membranes) using 50 mM LiPF_6 as the feed (1000 mL), 50 mM Na_2SO_4 as the anolyte (70 mL), and 100 mM LiOH (70 mL) as the catholyte.

permeation of OH^- from the feed through the AEM is unlikely due to the low activity of OH^- . Other possibilities are the H^+ permeation from the anolyte to the feed through the AEM or OH^- formation by water dissociation. H^+ permeation from anolyte may be due to imperfections of the AEM. Water dissociation is reported to occur on the fixed ionic groups at the surface of the membrane when a potential difference above a certain level is applied.^[48–50]

To identify the mechanism of pH decrease in the feed, electrodialysis was performed with saturated $\text{Ca}(\text{OH})_2$ added to the anolyte, keeping the pH at about 12. As shown in Figure 9, the pH of the feed decreased during electrodialysis. Since the pH of the feed decreased even when the anolyte was alkaline, the pH decrease may be due to dissociation of water on the AEM, not permeation from the anolyte. Additionally, a previous study reported that the limiting current density of electrodialysis for a 50 mM NaCl feed is $\approx 3\text{--}7 \text{ mA cm}^{-2}$.^[51] Compared to this value, the condition in this study exceeds the limiting current density, suggesting that water dissociation occurs. (Note: The previous studies used a Neosepta membrane, while this study uses a Selemion membrane. Both Neosepta and Selemion membranes are copolymers of styrene and divinylbenzene with sulfonate or quaternary ammonium groups, though their degree of polymerization and ion exchange group density may differ.) Therefore, water dissociation is assumed to be the dominant mechanism in this study.

Here, it is important to recognize that measuring the limiting current density is essential for determining appropriate operating conditions.^[52] Further investigation into water dissociation and membrane durability will be necessary to establish practically feasible electrodialysis conditions.

5.2. Permselectivity of PF_6^- and Cl^- in the AEM

To discuss the result for the permeation of PF_6^- and Cl^- shown in Figure 8a, two basic principles about diffusion in IEMs must

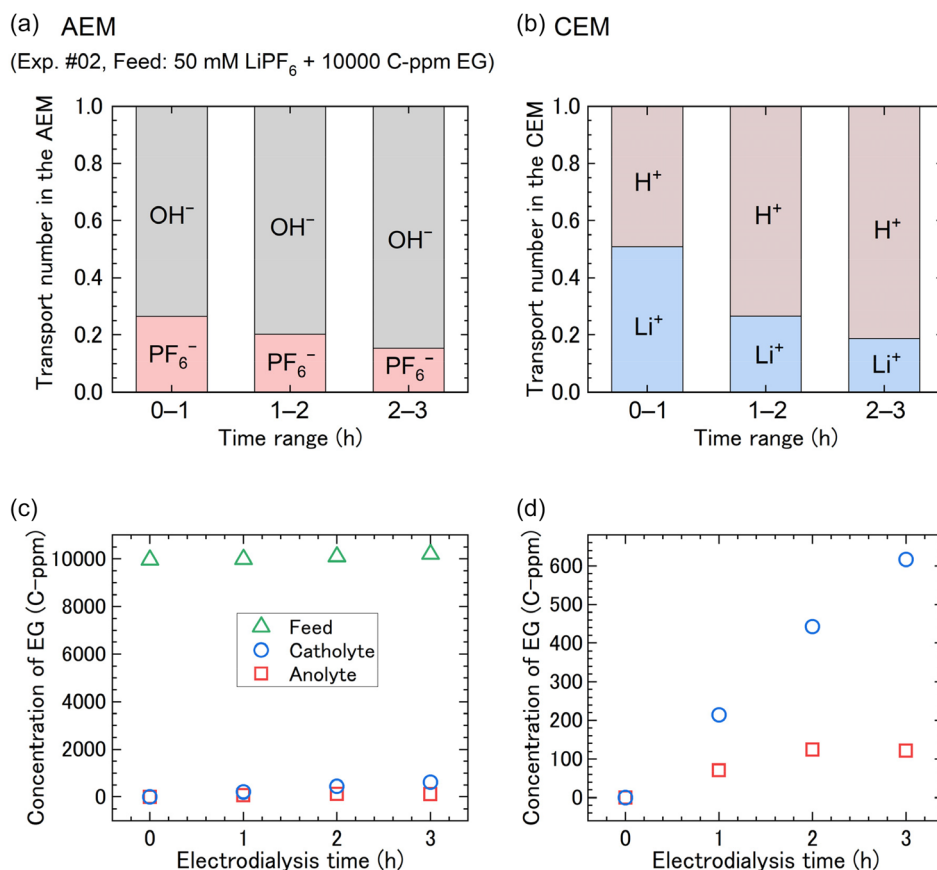


Figure 6. The transport numbers in a) the AEM and b) CEM, and c) the concentration changes of EG and d) enlarged view of (c) for exp. #02, where the electrodialysis was performed at 1000 mA (40 mA cm⁻² on the electrodes and 33 mA cm⁻² on the membranes) using 50 mM LiPF₆ + 10000 C-ppm EG as feed (1000 mL), 50 mM Na₂SO₄ as the anolyte (70 mL), and 100 mM LiOH (70 mL) as the catholyte.

be considered. First, the schematic illustration of the membrane structure and anion transport mechanism in the AEM is shown in **Figure 10**. Typical AEM consists of a gel phase and an interstitial phase. There are fixed cationic groups on the surface of a gel phase and anion. The electrical neutrality is satisfied by the sum of the charges of the fixed cationic groups and anions in the AEM. Anions are transferred in the interstitial phase or on fixed cationic groups by hopping.^[47,53] Among various anions, fast transfer using water molecules is possible only for OH⁻ like the Grotthuss mechanism of H⁺, resulting in larger diffusion coefficient than other anions.^[53–55]

Second, the transport of anions in the AEM follows the Nernst–Planck equation, expressed in Equation (6).^[56]

$$J_A^m = v^m C_A^m - D_A^m \frac{dC_A^m}{dx} - \frac{z_A F C_A^m D_A^m}{RT} \frac{d\varphi^m}{dx} \quad (6)$$

Here, J_A^m [kmol s⁻¹ m⁻²] is the flux of anion A at membrane m , v^m [m s⁻¹] is convective velocity of the solvent, C_A^m [mol L⁻¹] is the concentration of anion A in membrane m , D_A^m [m² s⁻¹] is diffusion coefficient of anion A in membrane m , z_A is valence of anion A, R (= 8.314 J mol⁻¹ K⁻¹) is the gas constant, T [K] is temperature, and $\frac{d\varphi^m}{dx}$ [V m⁻¹] is potential gradient in membrane m in the normal direction to membrane. When an external voltage is

applied between both sides of the AEM, the contribution of electromigration in the third term is greater, in which the convective transport in the first term and ion diffusion due to the concentration gradient in the second term are assumed to be negligible.^[42] In view of the third term in Equation (6), the permselectivity of several anions is determined by the diffusion coefficient and concentration of each anion in the AEM.

Based on the two basic principles mentioned above, the permselectivity of PF₆⁻ and Cl⁻ in the AEM is discussed. The permselectivity of different anions in the AEM was reported to correlate with the Gibbs energy of hydration (ΔG_H) of anions and Hofmeister anion series^[57,58] rather than the ionic Stokes radius.^[42,59,60] When the anions adsorb to the fixed cationic groups in the AEM, dehydration of some hydrated water molecules of anions is necessary. Therefore, the anion with negatively lower ΔG_H (more hydrophobic anion) occupies a larger number of fixed cationic groups in the AEM than one with negatively higher ΔG_H .^[61] In addition, the more hydrophobic anion adsorbs more strongly to the fixed cationic groups, resulting in the lower diffusion coefficient. The ΔG_H of PF₆⁻ was not reported as far as we know, but according to the reported Hofmeister anion series, the hydrophobicity of anions is estimated in order as follows: (hydrophilic) Cl⁻, NO₃⁻, BF₄⁻, ClO₄⁻, PF₆⁻ (hydrophobic).^[62,63] This tendency suggests that PF₆⁻ occupies

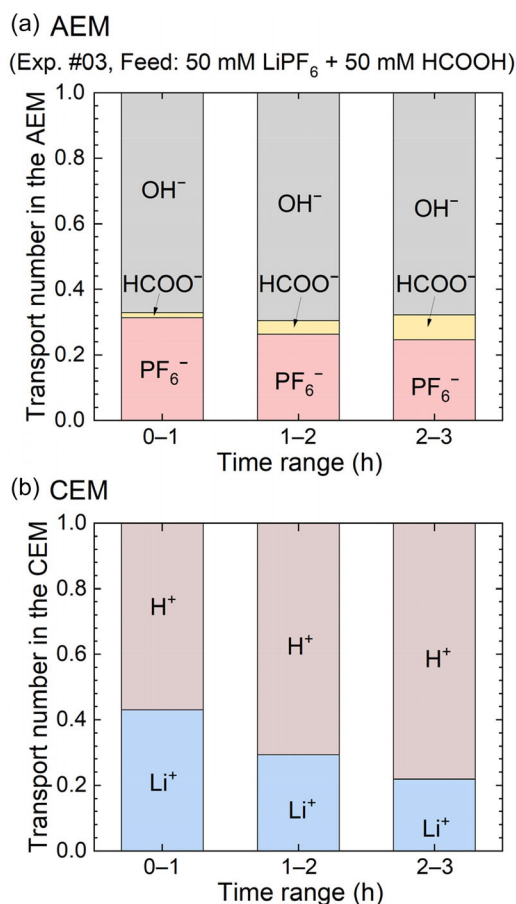


Figure 7. The transport numbers in a) the AEM and b) CEM for exp. #03, where electrodialysis was performed at 1000 mA (40 mA cm⁻² on the electrodes and 33 mA cm⁻² on the membranes) using 50 mM LiPF₆ + 50 mM HCOOH as the feed (1000 mL), 50 mM Na₂SO₄ as the anolyte (70 mL), and 100 mM LiOH (70 mL) as the catholyte.

a larger number of fixed cationic groups and has lower diffusion coefficient in the AEM than Cl⁻. To simplify the discussion, the diffusion coefficient of OH⁻ in the AEM is assumed to be sufficiently higher than that of Cl⁻ or PF₆⁻, so that the concentration of OH⁻ in the AEM can be assumed to be lower than that of Cl⁻ or PF₆⁻ and can be regarded as constant. Based on this assumption, the expected compositions of anions adsorbed to the fixed cationic groups on the gel phase of the AEM for each electrolyte solution are qualitatively shown in Figure 11. When PF₆⁻ and Cl⁻ permeate the AEM singly (exp. #01 and #04), these concentrations are determined by the number of fixed cationic groups and therefore expected to be as shown in Figure 11 (a) and (b). The difference in transport numbers between PF₆⁻ and Cl⁻ (exp. #01 and #04) is explained by the order of diffusion coefficient, PF₆⁻ < Cl⁻ as explained below. In the case of constant current electrolysis, the lower the diffusion coefficient of the anion, the higher the potential difference applied. The higher potential difference increases the amount of OH⁻ produced by the dissociation of water, resulting in a higher OH⁻ transport number. On the other hand, when PF₆⁻ and Cl⁻ permeate the AEM simultaneously (exp. #05), the concentration of

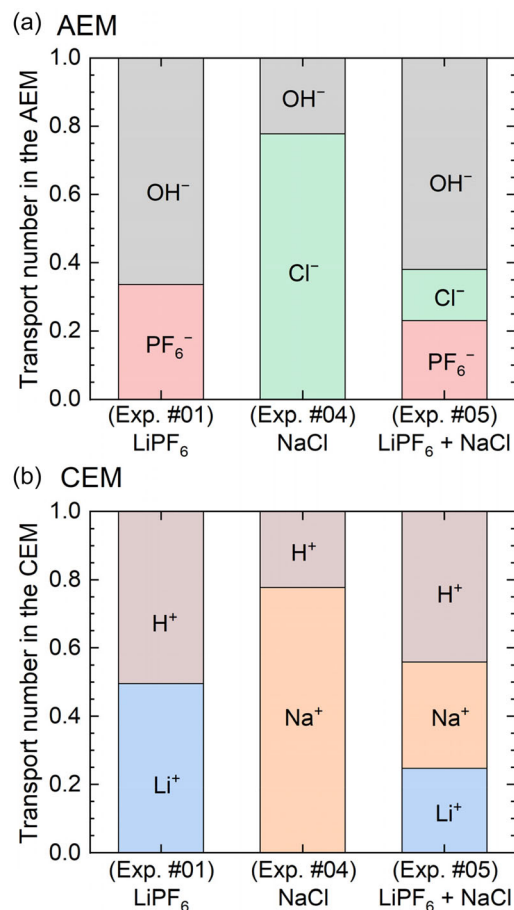


Figure 8. The transport numbers in a) the AEM and b) CEM at electrodialysis time range 0–1 when 50 mM LiPF₆ (exp. #01), 50 mM NaCl (exp. #04), and 50 mM LiPF₆ + 50 mM NaCl (exp. #05) were used as the feeds. The pH of the feed after 0–1 h of electrodialysis time range for exp. #01, #04, and #05 was 2.2, 3.3, and 1.9, respectively.

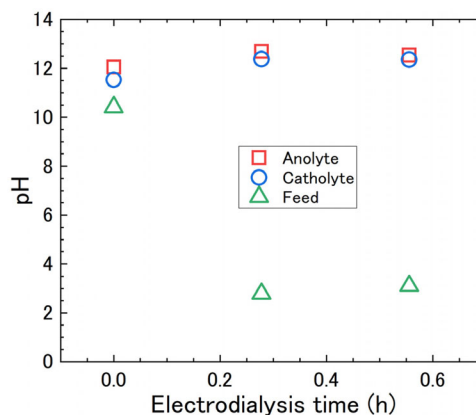


Figure 9. Measured pH when electrodialysis was performed at 1000 mA (40 mA cm⁻² on the electrodes and 33 mA cm⁻² on the membranes) using 100 mM LiPF₆ (200 mL), 500 mM Ca(OH)₂ (200 mL), and 100 mM LiOH (200 mL) as the feed, anolyte, and catholyte, respectively.

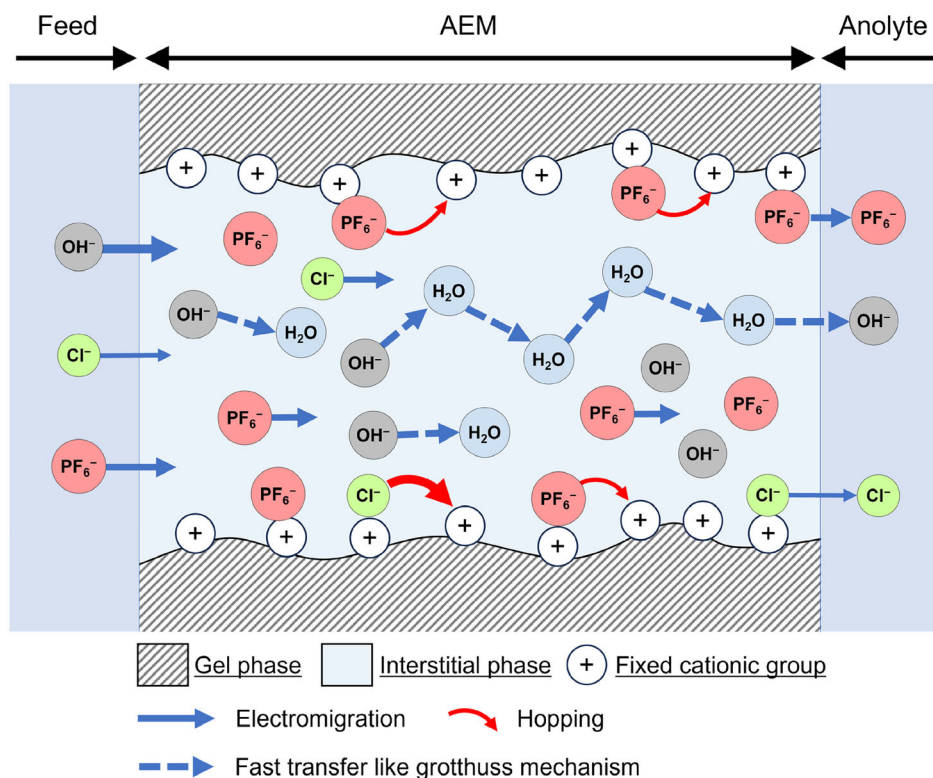


Figure 10. Schematic illustration of the membrane structure and the transport mechanism of anions in AEM.

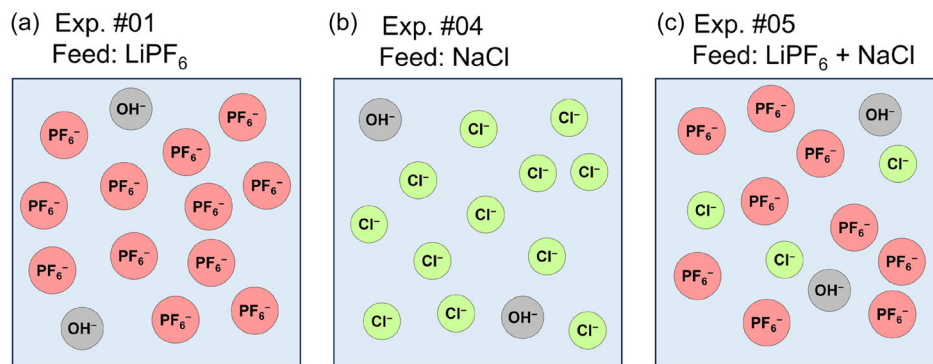


Figure 11. Schematic illustrations of possible anion compositions adsorbed to the fixed cationic groups on the gel phase of the AEM for a) exp. #01, b) #04, and c) #05. The fixed cationic groups are omitted, and electroneutrality is satisfied in the AEM.

PF_6^- is higher than that of Cl^- as shown in Figure 11 (c). As indicated by the Nernst–Planck equation (Equation (6)), the partial current of anion is determined by the product of its concentration and diffusion coefficient. The small transportation number of Cl^- for exp. #05 can be attributed to its low concentration in the AEM.

5.3. Operating Cost of Wastewater Treatment by Electrodialysis

For the wastewater treatment of LiPF_6 , the HCl addition method was reported previously,^[23] and the electrodialysis method is

proposed in this article. The operating costs of these methods are compared. In the HCl addition method, it is assumed that HCl is added into 200 L (water volume of the crushing facility in our previous reports^[15]) of wastewater containing 50 mm LiPF_6 at a concentration of 3 wt% HCl, and the temperature is raised to 90 °C for decomposition of PF_6^- . In the electrodialysis method, the wastewater is assumed to be concentrated to 500 mm HPF_6 in 20 L, and the decomposition is performed by raising the temperature of the wastewater to 90 °C. It is noted that an addition of acid is not necessary in electrodialysis because anodic reaction produces protons. After the decomposition in

Table 2. The comparison between the HCl addition method and the electrodialysis method for wastewater treatment of PF_6^- with original 200 L volume.

	Method	HCl addition	Electrodialysis
Wastewater ^{a)}	Concentration of LiPF_6 [mM]	50	500
	Volume of wastewater [L]	200	20
Cost	HCl cost [\$] ^{b)}	2.2 [19 kg]	–
	Electrodialysis cost [\$] ^{c)}	–	2.4–
	Heating cost [\$] ^{d)}	11–	1.0–
	$\text{Ca}(\text{OH})_2$ cost [\$] ^{b,e)}	1.4 [10 kg]	0.53 [3.7 kg]
	Total cost [\$]	15–	4.0–
Residual solution		$\text{CaCl}_2 + \text{LiCl}$	Deionized water

^{a)}Assumes that 200 L of wastewater containing 50 mM PF_6^- is concentrated by electrodialysis to 20 L of wastewater containing 500 mM PF_6^- . ^{b)}Reagent costs are based on August 2024 data from Japan's Ministry of Economy, trade and industry, Current Survey of Production, assuming 140 yen to the dollar.^[64] 35% HCl is assumed to be used to prepare 3 wt% HCl in wastewater.^[23] ^{c)}Referring to the results of this study, it is assumed that the cell voltage is 11 V, and the rate of ion separation is 100 h mol^{-1} when electrodialysis is performed at a current of 1 A. Electricity rate is assumed to be \$ 0.2 kWh^{-1} . ^{d)}Temperature is increased from 25 °C to 90 °C, assuming specific heat of wastewater is 4 kJ kg^{-1} , $10 \text{ MJ} = 1 \text{ kWh}$, and electricity rate is \$ 0.2 kWh^{-1} . The weight of the wastewater to be heated is 219 kg for the HCl addition method and 20 kg for the electrodialysis method. The calculated cost is a lower limit because heat dissipation is not taken into account. ^{e)}Sum amounts of $\text{Ca}(\text{OH})_2$ to precipitate PO_4^{3-} and F^- as hydroxylapatite and fluorite calculated using PHREEQC version 2 (see Supporting Information [N]).

both methods, precipitation removal of P and F is performed by adding a saturated amount of $\text{Ca}(\text{OH})_2$. Table 2 shows the assumed running costs for the HCl addition method and electrodialysis method. Note that the costs shown are only those derived from the chemical agents, heating for raising the temperature, and electrodialysis and do not take into account the heat loss due to heat dissipation, labor cost, the depreciation cost of the equipment investment, and so on. A comparison of these costs shows that the majority of the cost is accounted for by the heating cost. Treatment by electrodialysis reduces the amount of liquid that needs to be heated, and thus heat costs can be significantly reduced. Other advantages of electrodialysis method exist beyond cost. The solution remaining after treatment is a mixture of CaCl_2 and LiCl in the case of treatment with hydrochloric acid. This solution has limited industrial reuse applications because it contains Ca^{2+} causing scale formation and Cl^- promoting corrosion, in addition to the fact that Li recovery is not achieved. On the other hand, in electrodialysis, most of the wastewater is desalted, and the water is possible to be reused. Furthermore, the electrodialysis cost in Table 2 refers to the experimental results in this work, so the cost could be further reduced depending on the operating conditions. For example, bipolar electrodialysis, as shown in Figure 1 (b), can reduce cell voltage. Water dissociates at a lower potential difference at the BPM than that required for the hydrogen and oxygen evolution reactions on the electrodes.

6. Conclusion

In this study, the concentration and separation of PF_6^- and Li^+ by electrodialysis of wastewater containing LiPF_6 were attempted for PF_6^- wastewater treatment and Li^+ recovery. The solution of 50 mM LiPF_6 was prepared as the feed, and PF_6^- and Li^+ were transferred to the anolyte through the AEM and the catholyte through the CEM. Electrodialysis was performed at a constant current of 1000 mA (33 mA cm^{-2} on the membranes), and the transport numbers of PF_6^- at an AEM and Li^+ at a CEM were 0.22–0.32 and 0.20–0.50, respectively. The rest of the charge transfer is estimated to be carried by OH^- at an AEM and H^+ at a CEM. The small amounts of EG and formic acid permeated the AEM and the CEM, but the PF_6^- and Li^+ separations by electrodialysis were not significantly affected by them.

In order to investigate the transport chemistry of LiPF_6 in electrodialysis, it was compared with electrodialysis of NaCl solution. While the transport number of Cl^- in the AEM is greater than PF_6^- in case of the single permeation of each anion, the transport number of Cl^- is lower than PF_6^- in case simultaneous permeation of these anions. This difference in transport numbers was explained by the difference in the hydrophobicity of anions. A more hydrophobic anion tends to adsorb more strongly to the fixed cationic groups in the AEM, resulting in larger occupation of fixed cationic groups and lower diffusion coefficient in the AEM. Since PF_6^- is more hydrophobic than Cl^- , the smaller diffusion coefficient of PF_6^- results in a smaller transport number in single permeation, but in simultaneous permeation, PF_6^- suppresses the permeation of Cl^- because of the larger occupation of fixed cationic groups.

Finally, we estimated the amount of cost reduction by electrodialysis for the treatment of LiPF_6 wastewater. The results showed that there is potential for electrodialysis to significantly reduce the cost of wastewater treatment and achieve recycling of wastewater.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors have filed a patent covering the process described in this manuscript to Japanese Patent Application. Patent applicant: Kyoto University. Name of inventors: Takuto Miyashita, Kouji Yasuda and Tetsuya Uda. Application number: 2024-033205.

Author Contributions

All authors conceived the ideas. **Takuto Miyashita** contributed to the execution of the experiments, wrote the manuscript, and performed the analysis. All authors reviewed the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electrodialysis, ion exchange membranes, lithium-ion batteries, recycling, wastewater treatments

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